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## (54) RARE EARTH-IRON-BORON PERMANENT MAGNET MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To improve the magnetic characteristics of a rare earth-Fe-B perma nent magnet deteriorated by the cutting or electroplating process by post-heat treating it after forming an anticorrosive film.

SOLUTION: After forming an anticorrosive film on the surface of a sintered magnet composed of R (= one or more rare earth elements including Y) 20-45wt.%, Fe 50-80wt.%, Co 0.1-15wt.%, B 0.5-6wt.%, Cu 5wt.% or less and M (= at least one of Al, Si, Nb, Mo, V, Mn, Sn, Ni, Zn, Ti, Cr, Ta, W, Ge, Zr, Hf and Ga) 10wt.% or less, it is heat treated in an inert gas or nonoxidating atmosphere or vacuum at 400-600 deg.C to form a rare earth-iron-born permanent magnet. The anticorrosive film is a single or multilayer film composed of one or more elements selected among Zn, Cr, Ni, Cu, Sn, Pb, Cd, Ti, W, Co, Al and Ta.

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CLAIMS

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[Claim(s)]
[Claim 1] R (R is one sort or two sorts or more in the rare earth elements containing Y) 20-45wt.%, 0.1-15wt.% and B 0.5-6wt.%, [ Fe ] [ 50-80wt.% and Co ] The manufacture approach of the rare earth-iron-boron system permanent magnet characterized by heat-treating at the temperature of 400-600 degrees C among an inert gas ambient atmosphere, a non-oxidizing atmosphere, or a vacuum after Cu forms a corrosion-resistant coat in the sintered magnet body surface which consists below of 5wt(s).%.
[Claim 2] R (R is one sort or two sorts or more in the rare earth elements containing Y) 20-45wt.%, 0.1-15wt.% and B 0.5-6wt.%, [ Fe ] [ 50-80wt.% and Co ] Cu -- below 5wt(s).% and M (M -- aluminum, Si, Nb, Mo, and V --) Mn, Sn, nickel, Zn, Ti, Cr, Ta, W, germanium, Zr, Hf, The manufacture approach of the rare earth-iron-boron system permanent magnet characterized by heat-treating at the temperature of 400-600 degrees C among an inert gas ambient atmosphere, a non-oxidizing atmosphere, or a vacuum after one sort or two sorts or more in Ga form a corrosion-resistant coat in the sintered magnet body surface which consists below of 10wt(s).%.
[Claim 3] The manufacture approach of a rare earth-iron-boron system permanent magnet according to claim 1 or 2 that a corrosion-resistant coat consists of one sort or two sorts or more of elements among Zn, Cr, nickel, Cu, Sn, Pb, Cd, Ti, W, Co, aluminum, and Ta.
[Claim 4] The manufacture approach of a rare earth-iron-boron system permanent magnet according to claim 1 or 2 that a corrosion-resistant coat becomes at least one sort or two sorts or more of elements of C, P, S, O, B, and H from at least one sort or two sorts or more of elements among Zn, Cr, nickel, Cu, Sn, Pb, Cd, Ti, W, Co, aluminum, and Ta.
[Claim 5] The manufacture approach of a rare earth-iron-boron system permanent magnet given in claim 1 thru/or any of 4 they are. [ whose corrosion-resistant coat is monolayer with a thickness of 10 micrometers or more ]
[Claim 6] The manufacture approach of claim 1 characterized by for corrosion-resistant coats being multilayers, for the thickness of the coat which touches a magnet object being 0.1 micrometers or more, and the thickness of multilayers being 10 micrometers or more thru/or a rare earth-iron-boron system permanent magnet given in 4.
[Claim 7] The manufacture approach of the rare earth-iron-boron system permanent magnet according to claim 1 or 2 which forms a corrosion-resistant coat further after heat treatment.

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[Translation done.]

## DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] By performing the postheat treatment which formed the corrosion-resistant coat in the rare earth-iron-boron system permanent magnet, this invention improves degradation of the magnetic properties by cutting or electrolysis plating, and relates to the manufacture approach of the rare earth-iron-boron system permanent magnet which also raised the adhesion of a coat and a magnet object.
[0002]
[Description of the Prior Art] In recent years, in connection with small [ of electronic equipment or a precision mechanical equipment ], and the commercial-scene inclination of lightweight-izing, a rare earth magnet has come to be used in many fields instead of a conventional Alnico alloy and a conventional ferrite magnet in a permanent magnet. The need of the rare earth-iron-boron system permanent magnet with which a high energy product is especially acquired also in a rare earth permanent magnet is increasing, and it is in the inclination to be a high energy product more than before, and for high coercive force to be required. However, since this rare earth-iron-boron system permanent magnet has a low Curie temperature, it has the fault in which the temperature coefficient of a residual magnetic flux density carries out elevated-temperature demagnetization greatly. Moreover, it also has the fault of being easy to rust since the rare earth elements and iron which are easy to oxidize are used as the principal component. In order to conquer this low corrosion resistance, the approach of adding elements, such as Co, Ga, nickel, and Cr, is proposed variously.
[0003]
[Problem(s) to be Solved by the Invention] However, even if it is the rare earth-iron-boron system permanent magnet which added these elements, perfect corrosion resistance cannot be given. Therefore, if the rare earth-iron-boron system permanent magnet which does not have a corrosion-resistant coat is built into magnetic circuits, such as electronic equipment, oxidation will occur from a magnet body surface and will advance inside a magnet object. Consequently, magnetic properties deteriorate, engine performance, such as electronic equipment, is reduced or contamination by the magnetic substance to a peripheral device occurs according to omission of the oxide of a magnet body surface. By such reason, in order to prevent oxidation of a rare earth-iron-boron system permanent magnet body surface, various kinds of surface treatment approaches are proposed. For example, there is the electrolysis galvanizing method or nonelectrolytic plating method for galvanizing a metal or alloys, such as a vapor-plating method by the resin paint by the spray or electropainting, vacuum deposition, ion sputtering, and ion plating, and Cr, nickel. Among these, by the electrolysis galvanizing method or the nonelectrolytic plating method, in order to perform cleaning or activation by alkali or the acid etc. as pretreatment of plating, the layer in which the grain boundary phase which bears coercive force from a magnet body surface part at the time of pretreatment was eluted, consequently magnetic properties deteriorated in the magnet body surface section generates, and the magnetic properties of a magnet object fall. Especially, with a thin magnet, there is a trouble that the rate of degradation in magnetic properties becomes large.
[0004] Moreover, although it is necessary to carry out cutting of the whole surface or the necessary front face of a magnet object before coating in order to build a rare earth-iron-boron system permanent magnet object into electronic equipment, a magnet body surface is damaged also at this time, a processing degradation layer generates, and magnetic properties fall. And when coating is performed on this processing degradation layer, it becomes easy to generate coating exfoliation in a part for this processing degradation layer, and there is a trouble that the adhesion of coating also worsens. In order to improve degradation of the magnetic properties accompanying such cutting etc., after forming the alloy thin film layer of metallic elements, such as Ti and W, and rare earth elements, such as Ce, La, and Nd, by vapor-plating methods, such as vacuum deposition and ion sputtering, carrying out 400-900 degrees C and heat treatment of 1 minute - 3 hours in a vacuum or an inert atmosphere is proposed (JP,62-192566,A). However, since activity rare earth elements are included more than 50at(s).%, while corrosion resistance is bad, it becomes in cost and high. Moreover, there is also a trouble that coating to an inner hole and a slot cannot be performed. By JP,63-211703,A, in order to raise corrosion resistance, the adhesion force, and abrasion resistance, after forming the alloy layer of nickel-P by electroplating or the nonelectrolytic plating method, the temperature of 100-500 degrees C and the approach of carrying out heat treatment of 10 minutes - several hours are proposed, and after forming a nickel-P plating layer also in the example, the approach of heat-treating at the temperature of 150 or 180 degrees C is shown. However, in heat treatment at the temperature of about 200 degrees C generally known as an approach for removing the hydrogen by which occlusion was carried out to plating etc. like this example, since it is lower than the temperature which the liquid phase of R-rich equality generates, degradation of the magnetic properties by cutting etc. can be recovered, or adhesion of a magnet object and a plating layer cannot be raised. Moreover, in heat treatment of about 200 degrees C, there is a trouble of reducing magnetic properties on the contrary. In JP,1-139705,A, carrying out the laminating of noble-metals layers, such as Pd and Pt, and the base-metal layers, such as nickel, to a magnet body surface for the purpose of the improvement in adhesion with the anti-oxidation sex skin film and a magnet object, and carrying out diffusion heat treatment at 400-700 degrees C is proposed. However, by the approach of making the vapor-plating method or noble-metals colloid which forms noble metals, such as Pd and Pt, in a magnet body surface by the thickness of 10-100A adsorbing, a noble-metals layer tends to become porosity that it is easy to become an ununiformity. Therefore, it becomes easy to generate a pinhole in the base-metal layer which this attaches on it owing to, and corrosion resistance falls. Moreover, noble metals also have the trouble of becoming in cost and high. There is the approach of adding Co element which is an element which makes Curie temperature high as an approach of, decreasing the irreversible demagnetizing factor under hot environments like 160 degrees C on the other hand, and raising thermal stability. Moreover, it is known that Co addition will raise corrosion resistance. However, when Co element is added, there is a trouble that the heat-treatment-temperature range which gives the optimal coercive force becomes narrow, and mass-production nature worsens. Then, while this invention improves corrosion resistance and a temperature coefficient by adding Co element, it adds Cu element in order to extend the optimal

heat-treatment-temperature range which became narrow by Co addition, and it raises mass-production nature The fall of the magnetic properties by the corrosion-resistant coat formation to a sintered magnet body surface is prevented, and it aims at offering the manufacture approach of the rare earth-iron-boron system permanent magnet which raised the adhesion of a corrosion-resistant coat and a sintered magnet object.

[0005]

[Means for Solving the Problem] The manufacture approach of this permanent magnet for solving the above-mentioned technical problem R (R is one sort or two sorts or more in the rare earth elements containing Y) 20-45wt.%, 0.1-15wt.% and B 0.5-6wt.%, [ Fe ] [ 50-80wt.% and Co ] After Cu forms a corrosion-resistant coat in the sintered magnet body surface which consists below of 5wt(s).%, The manufacture approach of the rare earth-iron-boron system permanent magnet characterized by heat-treating at the temperature of 400-600 degrees C among an inert gas ambient atmosphere, a non-oxidizing atmosphere, or a vacuum, R (R is one sort or two sorts or more in the rare earth elements containing Y) Or 20-45wt.%, 0.1-15wt.% and B 0.5-6wt.%, [ Fe ] [ 50-80wt.% and Co ] Cu -- below 5wt(s).% and M (M -- aluminum, Si, Nb, Mo, and V --) Mn, Sn, nickel, Zn, Ti, Cr, Ta, W, germanium, Zr, Hf, After one sort or two sorts or more in Ga form a corrosion-resistant coat in the sintered magnet body surface which consists below of 10wt(s).%, It is the manufacture approach of the rare earth-iron-boron system permanent magnet characterized by heat-treating at the temperature of 400-600 degrees C among an inert gas ambient atmosphere, a non-oxidizing atmosphere, or a vacuum. Said corrosion-resistant coat Zn, Cr, nickel, Cu, Sn, Pb, Cd, Ti, The monolayer which consists of one sort or two sorts or more of elements among W, Co, aluminum, and Ta, multilayers, or said corrosion-resistant coat At least one sort or two sorts or more of elements of C, P, S, O, B, and H, It is desirable to consider as the monolayer or multilayers which consists of at least one sort or two sorts or more of elements among Zn, Cr, nickel, Cu, Sn, Pb, Cd, Ti, W, Co, aluminum, and Ta. this invention -- setting -- a corrosion-resistant coat -- monolayer or multilayers -- any are sufficient. Thickness of a coat is set to 10 micrometers or more when considering as monolayer. Moreover, when considering as multilayers, it is desirable to set to 0.1 micrometers or more thickness of the coat which touches a magnet object, and to set thickness of the corrosion-resistant whole coat to 10 micrometers or more. Moreover, in this invention, in order to raise the adhesion of a magnet object and a corrosion-resistant coat, it is desirable to pretreat cleaning of a magnet body surface, activation, etc. before corrosion-resistant coat formation.

[0006]

[Function] By performing the postheat treatment which formed the corrosion-resistant coat in the rare earth-iron-boron system permanent magnet which made the temperature coefficient of a residual magnetic flux density, and the corrosion resistance improvement, this invention improves degradation of the magnetic properties by cutting or electrolysis plating, and relates to the manufacture approach of the rare earth-iron-boron system permanent magnet which also raised the adhesion of the coating film and a magnet object. namely, the lattice defect which the magnitude of coercive force has in main phase R2F14B used as the bud of a reverse magnetic domain since the coercive force device of a rare earth-iron-boron system permanent magnet belongs to the new chestnut ESHON type and a rearrangement -- a number of -- it is -- it is determined by the crystalline structure, an amount, etc. surrounding main phase R2F14B considered to carry out pinning of the bud of a reverse magnetic domain of a grain boundary phase. So, if a crack and distortion generate in the main phase by cutting or the main phase without a grain boundary phase is exposed, that it is easy to generate the bud of a reverse magnetic domain, it becomes, or it will be easy to move a magnetic domain wall, it will become, and coercive force will decline. Moreover, with pretreatment using the acid or alkali performed at the time of corrosion-resistant coat coating, since the grain boundary phase of a magnet body surface part is eluted, the coercive force of a magnet body surface part declines, consequently the magnetic properties in the whole magnet object also fall. Especially degradation of magnetic properties according to pretreatment of these cutting or plating with the magnet object of a split becomes large.

[0007] Then, this invention is what utilized for the grain boundary phase the rare earth rich phase which exists in a surplus, and B rich equality, and after it forms a corrosion-resistant coat, it relates to the manufacture approach of the rare earth-iron-boron system permanent magnet heat-treated at 400-600 degrees C among an inert atmosphere, a non-oxidizing quality ambient atmosphere, or a vacuum. The liquid phase of rare earth rich equality does not generate that heat treatment temperature is less than 400 degrees C, and the effectiveness of this invention is not acquired. For heat treatment temperature, it is the good better pile which is considered as 450 degrees C or more more. While this invention raises the temperature characteristic of a sintered magnet object, and corrosion resistance by making Co contain By heat-treating at the temperature whose coercive force the liquid phase appears and moreover improves after forming a corrosion-resistant coat It is the manufacture approach of a permanent magnet of making the interface of a magnet body surface part and a corrosion-resistant coat breathing out in part the rare earth rich phase which exists in a grain boundary, restoring the grain boundary phase part eluted with pretreatment of a part for the processing degradation layer generated by cutting, an acid, and alkali, and recovering magnetic properties. In this invention, thickness of a corrosion-resistant coat was set to 10 micrometers or more because it was it easy to form a pinhole that the thickness of a corrosion-resistant coat is less than 10 micrometers and exudation and sufficient corrosion resistance were not acquired for a rare earth rich phase from a pinhole by heat treatment. Moreover, since the smooth nature of a corrosion-resistant coat will fall if thickness exceeds 50 micrometers, as for the thickness of a corrosion-resistant coat, it is desirable to be referred to as 50 micrometers or less. Although monolayer is sufficient as a corrosion-resistant coat, it is desirable to consider as multilayers and to set to 0.1 micrometers or more thickness of the coat which touches a magnet object. By considering as multilayers, the pinholes penetrated from a corrosion-resistant coat front face to a magnet body surface can decrease in number, and the corrosion from a pinhole can be prevented. Moreover, since it becomes easy to generate a pinhole to the coat as for which a coat tends to become that the thickness of the coat which touches a magnet object is less than 0.1 micrometers thin with porosity and which it attaches on it owing to, as for the thickness of the coat which touches a magnet object, it is desirable to be referred to as 0.1 micrometers or more. A corrosion-resistant coat Zn, Cr, nickel, Cu, Sn, Pb, Cd, Ti, W, The monolayer which consists of one sort or two sorts or more of elements among Co, aluminum, and Ta, multilayers, or said corrosion-resistant coat At least one sort or two sorts or more of elements of C, P, S, O, B, and H, It is desirable to consider as the monolayer or multilayers which consists of at least one sort or two sorts or more of elements among Zn, Cr, nickel, Cu, Sn, Pb, Cd, Ti, W, Co, aluminum, and Ta. Although C, P, S, O, B, and H have microcrystal-izing and the effectiveness made amorphous and contribute a corrosion-resistant coat to corrosion-resistant improvement, as for the plating bath of P, it is more desirable to use C, S, O, B, and H, since it is easy to damage a magnet object. When forming a corrosion-resistant coat with electrolysis plating, nickel plating, nickel-S plating, and Cu plating are hard to damage a magnet object and are desirable.

[0008] Hereafter, the reason for limitation of this invention is shown. It is one sort or two sorts or more of combination of rare earth elements which contains Y although the rare earth elements R used for the permanent magnet of this invention occupy 20 - 45wt.%, the rare earth rich phase which is a nonmagnetic phase when alpha-Fe generates under by 20wt.%, and high coercive force is not acquired but 45wt.% is exceeded increases, and the permanent magnet of the property which the residual magnetic flux density fell and was excellent is not obtained. Therefore, the range of R of 20 - 45wt.% is desirable. if B is an essential element in the above-mentioned permanent magnet, rhombohedron structure serves as the main phase under by 0.5wt.%, and high coercive force is not

acquired but 6wt.% is exceeded -- B -- since a rich nonmagnetic phase increases and a residual magnetic flux density falls, the outstanding permanent magnet is not obtained. Therefore, the range of B of 0.5 - 6wt.% is desirable. Since high coercive force will not be acquired if it is an essential element in the above-mentioned permanent magnet, a residual magnetic flux density falls under by 50wt.% and Fe also exceeds 80wt.%, the range of Fe of 50 - 80wt.% is desirable. Effectiveness that it is required in order that Co may raise the temperature characteristic and corrosion resistance, and the addition of Co is sufficient by below 0.1wt(s).% is not acquired, but if 15wt.% is exceeded, coercive force will decline. Therefore, the addition of Co has the desirable range of 0.1 - 15wt.%. It is an element required in order that Cu may extend the optimal heat treatment temperature from which the optimal coercive force is acquired and may raise mass-production nature, and since a residual magnetic flux density falls above 5wt.%, below 5wt(s).% of Cu is desirable. Moreover, since the optimal heat treatment temperature can be made low by adding Cu, when heat-treating after giving a corrosion-resistant coat, crystallization of a corrosion-resistant coat can control some and is desirable. Moreover, in order to raise magnetic properties or a physical property of a permanent magnet object etc. nickel, Nb, Ta, W, aluminum, Ti, Zr, Si, Ga, Mo, V, One sort or two sorts or more of elements of Sn, Cr, Mn, Zn, germanium, and Hf may be added in the range below 10wt(s).%. The permanent magnet of this invention With the sintering anisotropy permanent magnet which anisotropy-ized the alloy powder of a crystalline substance with shaping among a magnetic field and which is obtained by carrying out an afterbaking join, the compound which has the crystal structure of the tetragonal system in the range whose diameter of average crystal grain is 1-50 micrometers is made into the main phase, and a maximum energy product amounts to 20 or more MGOes. After pretreating the rare earth-iron-boron system permanent magnet object acquired in this way with an acid or alkali solutions, such as a phosphoric acid and a sodium hydroxide, a corrosion-resistant coat is produced by the approach generally [ electrolysis plating, nonelectrolytic plating, a vapor-plating method, etc. ] learned. Then, it heat-treats at 400-600 degrees C among an inert atmosphere, a non-oxidizing atmosphere, or a vacuum. As the formation approach of a corrosion-resistant coat, a cost side and the electrolysis plating from the homogeneity of the thickness of film, and nonelectrolytic plating are desirable. Moreover, the formation postheat treatment of the corrosion-resistant coat can be carried out, and a corrosion-resistant coat can be formed further. Since it crystallizes by heat treatment and a corrosion-resistant coat becomes weak, reinforcement is also suppliable by forming a corrosion-resistant coat further after heat treatment. When forming a corrosion-resistant coat after heat treatment, after pretreating with an acid or alkali solutions, such as a phosphoric acid and a sodium hydroxide, a corrosion-resistant coat can be produced by the approach generally [ electrolysis plating, nonelectrolytic plating, a vapor-plating method etc. ] learned. Moreover, coats, such as a resin coat, may be formed.

[0009]

[Example] Hereafter, this invention is not limited by these examples although an example explains this invention concretely.

[0010] (Example 1) The RF dissolution of the magnet alloy which consists of Nd23.5wt.%, Pr7.0wt.%, Dy1.5wt.%, aluminum0.2wt.%, Nb0.6wt.%, B1.05wt.%, Co2.3wt.%, Ga0.1wt.%, Cu0.08wt.%, and the remainder Fe was carried out in the inert atmosphere, and the casting ingot was obtained. After fracturing this ingot below on 50mm square, inserted the fracture lump into the well-closed container, Ar gas was made to flow for 20 minutes, and it permuted by air, and the hydrogen gas of 1 kgf/cm2 ground mechanically after 2-hour processing, and it was made the powder whose mean particle diameter is 500 micrometers. This coarse powder was pulverized to the powder whose mean particle diameter is 5.0 micrometers using the jet mill. Filling up with these fines the shaping space formed by the dice and bottom punch, and carrying out orientation all over the magnetic field of about 10 kOe(s), pressing was carried out by 2 ton/cm2, and the Plastic solid was acquired. This Plastic solid was sintered on 1080 degrees C and the conditions of 2 hours, 900 degrees C and heat treatment of 1 hour were performed, and the permanent magnet was produced. The 10x11x8mm (the magnetization direction: 8mm) sample was started from this magnet object, after surface polish, it pretreated with the phosphoric acid and electrolysis nickel plating with an average thickness of 20 micrometers was performed using the Watts bath. After performing 460-520 degrees C and heat treatment of 1 hour for the sample in which this nickel plating film was formed, in Ar gas ambient atmosphere, change of the irreversible demagnetizing factor to whenever [ magnetic-properties and stoving temperature ] was measured. Change of the irreversible demagnetizing factor to whenever [ stoving temperature ] is shown in drawing 1 at change of the coercive force over heat treatment temperature, and drawing 2 . Sample heat-treated at 480 degrees C to Table 1 QUAD SEVASTIANV The adhesion reinforcement of nickel plating film to twist is shown. Drawing 1 shows high coercive force being stabilized by the example 1 which is an example of this invention in the range whose heat treatment temperature is 460-500 degrees C, and being obtained. Moreover, from drawing 2 , an example 1 is compared with the examples 2 and 3 of a comparison, and is understood that there is little decline in the irreversible demagnetizing factor in an elevated temperature.

[0011] (Example 1 of a comparison) The RF dissolution of the magnet alloy which consists of Nd23.5wt.%, Pr7.0wt.%, Dy1.5wt.%, aluminum0.2wt.%, Nb0.6wt.%, B1.05wt.%, Co2.3wt.%, Ga0.1wt.%, and the remainder Fe was carried out in the inert atmosphere, and the casting ingot was obtained. After fracturing this ingot below on 50mm square, inserted the fracture lump into the well-closed container, Ar gas was made to flow for 20 minutes, and it permuted by air, and the hydrogen gas of 1 kgf/cm2 ground mechanically after 2-hour processing, and it was made the powder whose mean particle diameter is 500 micrometers. This coarse powder was pulverized to the powder whose mean particle diameter is 5.0 micrometers using the jet mill. Filling up with these fines the shaping space formed by the dice and bottom punch, and carrying out orientation all over the magnetic field of about 10 kOe(s), pressing was carried out by 2 ton/cm2, and the Plastic solid was acquired. This Plastic solid was sintered on 1080 degrees C and the conditions of 2 hours, 900 degrees C and heat treatment of 1 hour were performed, and the permanent magnet was produced. The 10x11x8mm (the magnetization direction: 8mm) sample was started from this magnet object, after surface polish, it pretreated with the phosphoric acid and electrolysis nickel plating with an average thickness of 20 micrometers was performed using the Watts bath. After performing 500-550 degrees C and heat treatment of 1 hour for the sample in which this nickel plating film was formed, in Ar gas ambient atmosphere, change of the irreversible demagnetizing factor to whenever [ magnetic-properties and stoving temperature ] was measured. Change of the coercive force over heat treatment temperature is shown in drawing 1 . Sample heat-treated at 520 degrees C to Table 1 QUAD SEVASTIAN V The adhesion reinforcement of nickel plating film to twist is shown. From drawing 1 , the example 1 of a comparison is understood that change of the coercive force over heat treatment temperature is large.

[0012] (Example 2 of a comparison) The RF dissolution of the magnet alloy which consists of Nd23.5wt.%, Pr7.0wt.%, Dy1.5wt.%, aluminum0.2wt.%, Nb0.6wt.%, B1.05wt.%, Co2.3wt.%, Ga0.1wt.%, Cu0.08wt.%, and the remainder Fe was carried out in the inert atmosphere, and the casting ingot was obtained. After fracturing this ingot below on 50mm square, inserted the fracture lump into the well-closed container, Ar gas was made to flow for 20 minutes, and it permuted by air, and the hydrogen gas of 1 kgf/cm2 ground mechanically after 2-hour processing, and it was made the powder whose mean particle diameter is 500 micrometers. This coarse powder was pulverized to the powder whose mean particle diameter is 5.0 micrometers using the jet mill. Filling up with these fines the shaping space formed by the dice and bottom punch, and carrying out orientation all over the magnetic field of about 10 kOe(s), pressing was carried out by 2 ton/cm2, and the Plastic solid was acquired. This Plastic solid was sintered on 1080 degrees C and the conditions of 2 hours, 900 degrees C, 480 degrees C, and heat treatment of 1 hour were performed, and the permanent magnet was produced. The 10x11x8mm (the magnetization direction: 8mm) sample was started from this magnet object, after surface polish, it

pretreated with the phosphoric acid and electrolysis nickel plating with an average thickness of 20 micrometers was performed using the Watts bath. Change of the irreversible demagnetizing factor to whenever [ stoving temperature ] is shown in drawing 2 . To Table 1 QUAD SEVASTIAN V The adhesion reinforcement of nickel plating film to twist is shown. From drawing 2 , the example 1 which is an example of this invention is compared with the example 2 of a comparison, and is understood that the irreversible demagnetizing factor in an elevated temperature is good.

[0013]

[Table 1]

| | |
|---|---|
| 実施例1 | 530 kgf／cm2 |
| 比較例1 | 525 kgf／cm2 |
| 比較例2 | 30 kgf／cm2 |

[0014] (Example 3 of a comparison) The RF dissolution of the magnet alloy which consists of Nd23.5wt.%, Pr7.0wt.%, Dy1.5wt.%, aluminum0.2wt.%, Nb0.6wt.%, B1.05wt.%, Co2.3wt.%, Ga0.1wt.%, Cu0.08wt.%, and the remainder Fe was carried out in the inert atmosphere, and the casting ingot was obtained. After fracturing this ingot below on 50mm square, inserted the fracture lump into the well-closed container, Ar gas was made to flow for 20 minutes, and it permuted by air, and the hydrogen gas of 1 kgf/cm2 ground mechanically after 2-hour processing, and it was made the powder whose mean particle diameter is 500 micrometers. This coarse powder was pulverized to the powder whose mean particle diameter is 5.0 micrometers using the jet mill. Filling up with these fines the shaping space formed by the dice and bottom punch, and carrying out orientation all over the magnetic field of about 10 kOe(s), pressing was carried out by 2 ton/cm2, and the Plastic solid was acquired. This Plastic solid was sintered on 1080 degrees C and the conditions of 2 hours, 900 degrees C, 480 degrees C, and heat treatment of 1 hour were performed, and the permanent magnet was produced. The 10x11x8mm (the magnetization direction: 8mm) sample was started from this magnet object, after surface polish, it pretreated with the phosphoric acid and electrolysis nickel plating with an average thickness of 20 micrometers was performed using the Watts bath. After performing 200 degrees C and heat treatment of 1 hour for the sample in which this nickel plating film was formed, in Ar gas ambient atmosphere, change of the irreversible demagnetizing factor to whenever [ stoving temperature ] was measured. Change of the irreversible demagnetizing factor to whenever [ stoving temperature ] is shown in drawing 2 . The example 3 of a comparison which heat-treated at 200 degrees C after plating film formation has equivalent example 2 of a comparison and irreversible demagnetizing factor which do not heat-treat after plating film formation, and drawing 2 shows that the effectiveness of the improvement in an irreversible demagnetizing factor is not acquired in heat treatment it is [ heat treatment ] about 200 degrees C.

[Effect of the Invention] By according to this invention, forming a corrosion-resistant coat in the R-Fe-B system permanent magnet which raised the temperature characteristic and corrosion resistance, and heat-treating at 400-600 degrees C among an inert atmosphere, a non-oxidizing atmosphere, or a vacuum While making the crystalline-structure section which deteriorated with cutting or electrolysis plating restore and improving degradation of magnetic properties, and secular change of magnetic properties, the adhesion of the coating film and a magnet object can also be raised and the utility value is very high on industry.

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[Translation done.]

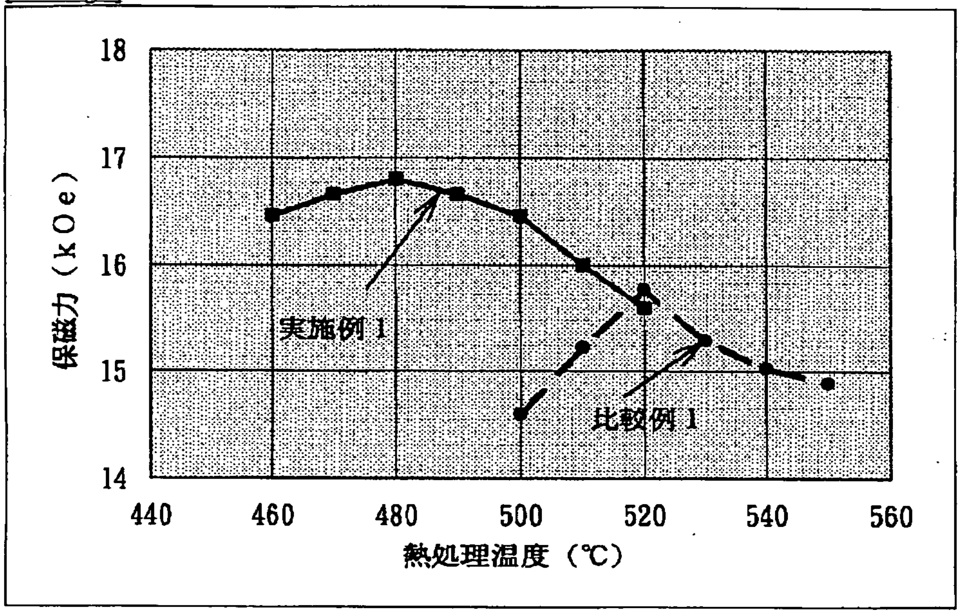
## DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing showing change of the coercive force over the heat treatment temperature after plating film formation.
[Drawing 2] It is drawing showing change of the irreversible demagnetizing factor to whenever [ stoving temperature ].

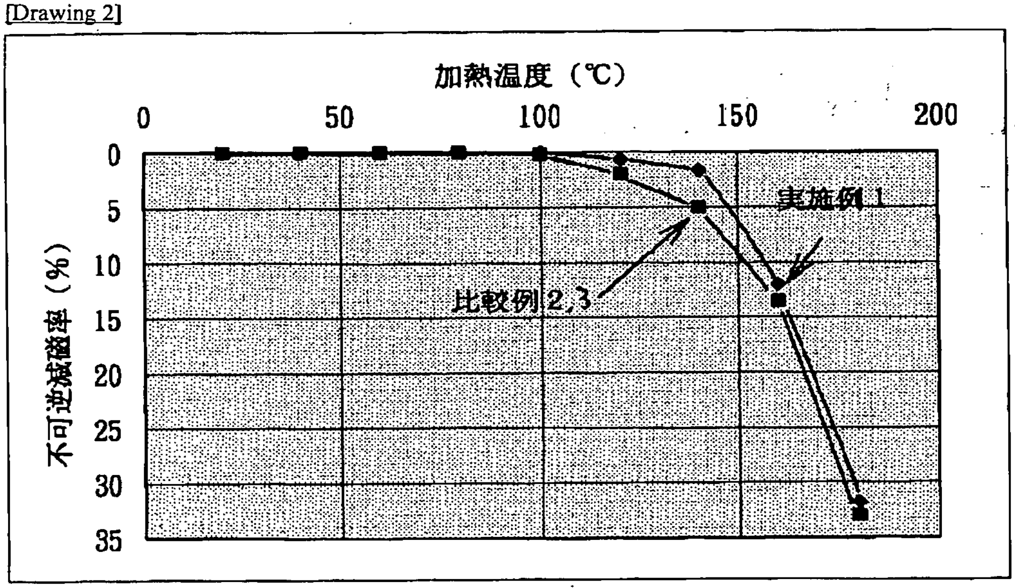
[Translation done.]

DRAWINGS

[Drawing 1]




[Drawing 2]

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(54)【発明の名称】　希土類－鉄－ボロン系永久磁石の製造方法

(57)【要約】

【目的】　本発明の目的は、Ｃｏ元素を添加することにより耐食性及び温度係数を改善し、Ｃｏ添加により狭くなった最適熱処理温度範囲を広げるためにＣｕ元素を添加し量産性を向上させるとともに、焼結磁石体表面への耐食性皮膜形成による磁気特性の低下を防止し、耐食性皮膜と焼結磁石体との密着性を向上させた希土類－鉄－ボロン系永久磁石の製造方法を提供することである。

【構成】　本発明は、Ｒ（ＲはＹを含む希土類元素のうち１種または２種以上）が２０～４５ｗｔ．％、Ｆｅが５０～８０ｗｔ．％、Ｃｏが０．１～１５ｗｔ．％、Ｂが０．５～６ｗｔ．％、Ｃｕが５ｗｔ．％以下からなる焼結磁石体表面に耐食性皮膜を形成した後、不活性ガス雰囲気、非酸化性雰囲気あるいは真空中、４００～６００℃の温度で熱処理する希土類－鉄－ボロン系永久磁石の製造方法である。

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【特許請求の範囲】

【請求項１】　Ｒ（ＲはＹを含む希土類元素のうち１種または２種以上）が２０～４５ｗｔ．％、Ｆｅが５０～８０ｗｔ．％、Ｃｏが０．１～１５ｗｔ．％、Ｂが０．５～６ｗｔ．％、Ｃｕが５ｗｔ．％以下からなる焼結磁石体表面に耐食性皮膜を形成した後、不活性ガス雰囲気、非酸化性雰囲気あるいは真空中、４００～６００℃の温度で熱処理することを特徴とする希土類－鉄－ボロン系永久磁石の製造方法。

【請求項２】　Ｒ（ＲはＹを含む希土類元素のうち１種または２種以上）が２０～４５ｗｔ．％、Ｆｅが５０～８０ｗｔ．％、Ｃｏが０．１～１５ｗｔ．％、Ｂが０．５～６ｗｔ．％、Ｃｕが５ｗｔ．％以下およびＭ（ＭはＡｌ、Ｓｉ、Ｎｂ、Ｍｏ、Ｖ、Ｍｎ、Ｓｎ、Ｎｉ、Ｚｎ、Ｔｉ、Ｃｒ、Ｔａ、Ｗ、Ｇｅ、Ｚｒ、Ｈｆ、Ｇａのうち１種または２種以上）が１０ｗｔ．％以下からなる焼結磁石体表面に耐食性皮膜を形成した後、不活性ガス雰囲気、非酸化性雰囲気あるいは真空中、４００～６００℃の温度で熱処理することを特徴とする希土類－鉄－ボロン系永久磁石の製造方法。

【請求項３】　耐食性皮膜がＺｎ、Ｃｒ、Ｎｉ、Ｃｕ、Ｓｎ、Ｐｂ、Ｃｄ、Ｔｉ、Ｗ、Ｃｏ、Ａｌ、Ｔａのうち１種または２種以上の元素からなる請求項１または２に記載の希土類－鉄－ボロン系永久磁石の製造方法。

【請求項４】　耐食性皮膜がＣ、Ｐ、Ｓ、Ｏ、Ｂ、Ｈの少なくとも１種または２種以上の元素と、Ｚｎ、Ｃｒ、Ｎｉ、Ｃｕ、Ｓｎ、Ｐｂ、Ｃｄ、Ｔｉ、Ｗ、Ｃｏ、Ａｌ、Ｔａのうち少なくとも１種または２種以上の元素からなる請求項１または２に記載の希土類－鉄－ボロン系永久磁石の製造方法。

【請求項５】　耐食性皮膜が厚さ１０μｍ以上の単層膜である請求項１ないし４のいづれかに記載の希土類－鉄－ボロン系永久磁石の製造方法。

【請求項６】　耐食性皮膜が多層膜であって、磁石体と接する皮膜の膜厚が０．１μｍ以上であり、多層膜の膜厚が１０μｍ以上であることを特徴とする請求項１ないし４に記載の希土類－鉄－ボロン系永久磁石の製造方法。

【請求項７】　熱処理後、さらに耐食性皮膜を形成する請求項１または２に記載の希土類－鉄－ボロン系永久磁石の製造方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、希土類－鉄－ボロン系永久磁石に耐食性皮膜を形成した後熱処理を行うことにより、切削加工あるいは電解めっき等による磁気特性の劣化を改善し、皮膜と磁石体との密着性をも向上させた希土類－鉄－ボロン系永久磁石の製造方法に関するものである。

【０００２】

【従来の技術】近年、電子機器や精密機器の小型、軽量化の市場傾向に伴い、永久磁石においては従来のアルニコやフェライト磁石に代わり希土類磁石が多くの分野で利用されるようになってきた。希土類永久磁石の中でも、特に、高いエネルギー積が得られる希土類－鉄－ボロン系永久磁石の需要が増加しており、従来以上に高エネルギー積でかつ高保磁力が要求される傾向にある。しかしながら、この希土類－鉄－ボロン系永久磁石はキュリー温度が低いために残留磁束密度の温度係数が大きく高温減磁する欠点を有している。また、酸化しやすい希土類元素および鉄を主成分としているために錆びやすいという欠点も有している。この低耐食性を克服するために、Ｃｏ、Ｇａ、Ｎｉ、Ｃｒ等の元素を添加する方法が種々提案されている。

【０００３】

【発明が解決しようとする課題】しかしながら、これらの元素を添加した希土類－鉄－ボロン系永久磁石であっても、完全な耐食性を付与することはできない。従って、耐食性皮膜を有しない希土類－鉄－ボロン系永久磁石を電子機器等の磁気回路に組み込むと、酸化が磁石体表面から発生し磁石体内部に進行する。その結果、磁気特性が劣化し電子機器等の性能を低下させたり、磁石体表面の酸化物の脱落により周辺機器への磁性体による汚染が発生する。このような理由で、希土類－鉄－ボロン系永久磁石体表面の酸化を防止するために、各種の表面処理方法が提案されている。例えば、スプレーまたは電着塗装による樹脂塗装、真空蒸着、イオンスパッタリング、イオンプレーティングによる気相めっき法、Ｃｒ、Ｎｉ等の金属あるいは合金をめっきをする電解めっき法あるいは無電解めっき法がある。これらのうち、電解めっき法あるいは無電解めっき法では、めっきの前処理としてアルカリあるいは酸による脱脂あるいは活性化処理等を行うために、前処理時に磁石体表面部分から保磁力を担う粒界相が溶出し、その結果、磁石体表面部で磁気特性の劣化した層が生成し磁石体の磁気特性が低下する。特に、薄型の磁石では磁気特性における劣化の割合が大きくなるという問題点がある。

【０００４】また、希土類－鉄－ボロン系永久磁石体を電子機器に組み込むためには、コーティング前に磁石体の全面あるいは所要表面を切削加工する必要があるが、この時にも、磁石体表面が荒らされて加工劣化層が生成し磁気特性が低下する。そして、この加工劣化層の上にコーティングを施すと、この加工劣化層部分でコーティング剥離が発生しやすくなりコーティングの密着性も悪くなるという問題点がある。このような切削加工等に伴う磁気特性の劣化を改善するために、Ｔｉ、Ｗ等の金属元素とＣｅ、Ｌａ、Ｎｄ等の希土類元素との合金薄膜層を真空蒸着、イオンスパッタリング等の気相めっき法で形成した後、真空あるいは不活性雰囲気中で４００～９００℃、１分～３時間の熱処理をすることが提案されて

いる（特開昭６２－１９２５６６号）。しかしながら、活性な希土類元素を５０ａｔ．％以上含むために耐食性が悪いと同時に、コスト的にも高くなる。また、内穴、溝部へのコーティングができないという問題点もある。特開昭６３－２１１７０３号では、耐食性、密着力、耐磨耗性を向上させるために、電気めっき法あるいは無電解めっき法でＮｉ－Ｐの合金層を形成した後１００～５００℃の温度、１０分～数時間の熱処理をする方法が提案されており、実施例でもＮｉ－Ｐめっき層を形成した後１５０、１８０℃の温度で熱処理する方法が示されている。しかしながら、この実施例のようにめっき等に吸蔵された水素を除くための方法として一般的に知られた２００℃程度の温度での熱処理では、R-rich相等の液相が生成する温度よりも低いために切削加工等による磁気特性の劣化を回復させたり、磁石体とめっき層との密着性を向上させたりすることができない。また、２００℃程度の熱処理ではかえって磁気特性を低下させるという問題点がある。特開平１－１３９７０５号では、耐酸化性皮膜と磁石体との密着性向上を目的として、磁石体表面にＰｄ、Ｐｔ等の貴金属層と、Ｎｉ等の卑金属層とを積層し、４００～７００℃で拡散熱処理することが提案されている。しかしながら、Ｐｄ、Ｐｔ等の貴金属を１０～１００Åの膜厚で磁石体表面に形成する気相めっき法あるいは貴金属コロイドを吸着させる方法では、貴金属層は不均一になりやすく多孔性になりやすい。従って、これが原因でその上に付ける卑金属層にピンホールが発生しやすくなり耐食性が低下する。また、貴金属はコスト的にも高くなるという問題点もある。一方、１６０℃のような高温環境下での不可逆減磁率を減少させ熱安定性を向上させる方法として、キュリー温度を高くする元素であるＣｏ元素等を添加する方法がある。また、Ｃｏ添加は耐食性を向上させることが知られている。しかしながら、Ｃｏ元素を添加すると最適な保磁力を与える熱処理温度範囲が狭くなり量産性が悪くなるという問題点がある。そこで、本発明は、Ｃｏ元素を添加することにより耐食性及び温度係数を改善し、Ｃｏ添加により狭くなった最適熱処理温度範囲を広げるためにＣｕ元素を添加し量産性を向上させるとともに、焼結磁石体表面への耐食性皮膜形成による磁気特性の低下を防止し、耐食性皮膜と焼結磁石体との密着性を向上させた希土類－鉄－ボロン系永久磁石の製造方法を提供することを目的とする。

【０００５】

【課題を解決するための手段】上記課題を解決するための本永久磁石の製造方法は、Ｒ（ＲはＹを含む希土類元素のうち１種または２種以上）が２０～４５ｗｔ．％、Ｆｅが５０～８０ｗｔ．％、Ｃｏが０．１～１５ｗｔ．％、Ｂが０．５～６ｗｔ．％、Ｃｕが５ｗｔ．％以下からなる焼結磁石体表面に耐食性皮膜を形成した後、不活性ガス雰囲気、非酸化性雰囲気あるいは真空中、４００～６００℃の温度で熱処理することを特徴とする希土類－鉄－ボロン系永久磁石の製造方法、あるいはＲ（ＲはＹを含む希土類元素のうち１種または２種以上）が２０～４５ｗｔ．％、Ｆｅが５０～８０ｗｔ．％、Ｃｏが０．１～１５ｗｔ．％、Ｂが０．５～６ｗｔ．％、Ｃｕが５ｗｔ．％以下およびＭ（ＭはＡｌ、Ｓｉ、Ｎｂ、Ｍｏ、Ｖ、Ｍｎ、Ｓｎ、Ｎｉ、Ｚｎ、Ｔｉ、Ｃｒ、Ｔａ、Ｗ、Ｇｅ、Ｚｒ、Ｈｆ、Ｇａのうち１種または２種以上）が１０ｗｔ．％以下からなる焼結磁石体表面に耐食性皮膜を形成した後、不活性ガス雰囲気、非酸化性雰囲気あるいは真空中、４００～６００℃の温度で熱処理することを特徴とする希土類－鉄－ボロン系永久磁石の製造方法であり、前記耐食性皮膜がＺｎ、Ｃｒ、Ｎｉ、Ｃｕ、Ｓｎ、Ｐｂ、Ｃｄ、Ｔｉ、Ｗ、Ｃｏ、Ａｌ、Ｔａのうち１種または２種以上の元素からなる単層膜または多層膜、あるいは前記耐食性皮膜がＣ、Ｐ、Ｓ、Ｏ、Ｂ、Ｈの少なくとも１種または２種以上の元素と、Ｚｎ、Ｃｒ、Ｎｉ、Ｃｕ、Ｓｎ、Ｐｂ、Ｃｄ、Ｔｉ、Ｗ、Ｃｏ、Ａｌ、Ｔａのうち少なくとも１種または２種以上の元素からなる単層膜または多層膜とするのが好ましい。本発明において、耐食性皮膜は単層膜または多層膜いづれでもよい。単層膜とする場合、皮膜の厚さは１０μｍ以上とする。また、多層膜とする場合、磁石体と接する皮膜の膜厚を０．１μｍ以上とし、耐食性皮膜全体の厚さを１０μｍ以上とするのが好ましい。また、本発明においては、磁石体と耐食性皮膜との密着性を向上させるために耐食性皮膜形成前に磁石体表面の脱脂、活性化処理等の前処理を行うことが好ましい。

【０００６】

【作用】本発明は、残留磁束密度の温度係数および耐食性の改善を行った希土類－鉄－ボロン系永久磁石に耐食性皮膜を形成した後熱処理を行うことにより、切削加工あるいは電解めっき等による磁気特性の劣化を改善し、コーティング膜と磁石体との密着性をも向上させた希土類－鉄－ボロン系永久磁石の製造方法に関するものである。すなわち、希土類－鉄－ボロン系永久磁石の保磁力機構はニュークリエーションタイプに属しているために、保磁力の大きさは逆磁区の芽となる主相R2Ｆ１４Ｂ内にある格子欠陥や転位の数あるいは逆磁区の芽をピン止めしていると考えられる主相Ｒ２Ｆ14Ｂを囲む粒界相の結晶組織や量等により決定される。それゆえ、切削加工により主相内にクラックや歪みが生成したり、粒界相を持たない主相が露出すると、逆磁区の芽が発生しやすくなったり、磁壁が動きやすくなり保磁力が低下する。また、耐食性皮膜コーティング時に行う酸あるいはアルカリを用いた前処理では、磁石体表面部分の粒界相が溶出するために、磁石体表面部分の保磁力は低下し、その結果、磁石体全体での磁気特性も低下する。特に、薄物の磁石体ではこれら切削加工あるいはめっきの前処理による磁気特性の劣化は大きくなる。

【０００７】そこで、本発明は、粒界相に余剰に存在する希土類リッチ相、Ｂリッチ相等を活用したもので、耐食性皮膜を形成した後不活性雰囲気、非酸化性雰囲気あるいは真空中、４００～６００℃で熱処理する希土類−鉄−ボロン系永久磁石の製造方法に関するものである。熱処理温度が４００℃未満であると、希土類リッチ相等の液相が生成せず、本発明の効果は得られない。熱処理温度は４５０℃以上とするのが、より好ましくい。本発明は、Ｃｏを含有させることにより焼結磁石体の温度特性および耐食性を向上させるとともに、耐食性皮膜を形成した後液相が出現ししかも保磁力が向上する温度で熱処理することにより、粒界に存在する希土類リッチ相を磁石体表面部分と耐食性皮膜との界面に一部吐き出させ、切削加工により生成した加工劣化層部分あるいは酸、アルカリの前処理で溶出した粒界相部分を修復し磁気特性を回復させる永久磁石の製造方法である。本発明において、耐食性皮膜の厚さを１０μｍ以上としたのは、耐食性皮膜の厚さが１０μｍ未満であるとピンホールが形成しやすく、熱処理によりピンホールから希土類リッチ相がしみ出し、充分な耐食性が得られないからである。また、厚さが５０μｍを越えると耐食性皮膜の平滑性が低下するので、耐食性皮膜の厚さは５０μｍ以下とするのが好ましい。耐食性皮膜は単層膜でもよいが、多層膜とし、磁石体と接する皮膜の厚さを０．１μｍ以上とするのが好ましい。多層膜とすることにより、耐食性皮膜表面から磁石体表面に貫通するピンホールが減少し、ピンホールからの腐食を防止することができる。また、磁石体と接する皮膜の厚さが０．１μｍ未満であると皮膜が薄く多孔性となりやすく、それが原因でその上に付ける皮膜にピンホールが生成しやすくなるので、磁石体に接する皮膜の厚さは０．１μｍ以上とするのが好ましい。耐食性皮膜がＺｎ、Ｃｒ、Ｎｉ、Ｃｕ、Ｓｎ、Ｐｂ、Ｃｄ、Ｔｉ、Ｗ、Ｃｏ、Ａｌ、Ｔａのうち１種または２種以上の元素からなる単層膜または多層膜、あるいは前記耐食性皮膜がＣ、Ｐ、Ｓ、Ｏ、Ｂ、Ｈの少なくとも１種または２種以上の元素と、Ｚｎ、Ｃｒ、Ｎｉ、Ｃｕ、Ｓｎ、Ｐｂ、Ｃｄ、Ｔｉ、Ｗ、Ｃｏ、Ａｌ、Ｔａのうち少なくとも１種または２種以上の元素からなる単層膜または多層膜とするのが好ましい。Ｃ、Ｐ、Ｓ、Ｏ、Ｂ、Ｈは、耐食性皮膜を微結晶化、非晶質化する効果があり耐食性向上に寄与するが、Ｐのめっき浴は磁石体を傷めやすいのでＣ、Ｓ、Ｏ、Ｂ、Ｈを用いることが、より好ましい。電解めっきにより耐食性皮膜を形成する場合、Ｎｉめっき、Ｎｉ−Ｓめっき、Ｃｕめっきが磁石体を傷めにくく好ましい。

【０００８】以下、本発明の限定理由について示す。本発明の永久磁石に用いる希土類元素Ｒは、２０～４５ｗｔ．％を占めるが、Ｙを含む希土類元素の１種または２種以上の組合せであって、２０ｗｔ．％未満ではα−Ｆｅが生成し高保磁力が得られず、４５ｗｔ．％を超えると非磁性相である希土類リッチ相が多くなり、残留磁束密度が低下して優れた特性の永久磁石が得られない。よって、Ｒは２０～４５ｗｔ．％の範囲が好ましい。Ｂは、上記永久磁石における必須元素であって、０．５ｗｔ．％未満では菱面体構造が主相となり高保磁力が得られず、６ｗｔ．％を超えるとＢリッチな非磁性相が多くなり、残留磁束密度が低下するため、優れた永久磁石が得られない。よって、Ｂは０．５～６ｗｔ．％の範囲が好ましい。Ｆｅも、上記永久磁石において必須元素であり、５０ｗｔ．％未満では残留磁束密度が低下し、８０ｗｔ．％を超えると高保磁力が得られないので、Ｆｅは５０～８０ｗｔ．％の範囲が好ましい。Ｃｏは温度特性および耐食性を向上させるために必要であり、Ｃｏの添加量が０．１ｗｔ．％以下では十分な効果が得られず、１５ｗｔ．％を超えると保磁力が低下する。よって、Ｃｏの添加量は０．１～１５ｗｔ．％の範囲が好ましい。Ｃｕは、最適な保磁力が得られる最適熱処理温度を広げ量産性を向上させるために必要な元素であり、５ｗｔ．％以上では残留磁束密度が低下するのでＣｕは５ｗｔ．％以下が好ましい。また、Ｃｕを添加することにより、最適熱処理温度を低くすることができるので、耐食性皮膜を施した後に熱処理する場合には耐食性皮膜の結晶化が多少抑制することができ好ましい。また、永久磁石体の磁気特性あるいは物理特性等を向上させるために、Ｎｉ、Ｎｂ、Ｔａ、Ｗ、Ａｌ、Ｔｉ、Ｚｒ、Ｓｉ、Ｇａ、Ｍｏ、Ｖ、Ｓｎ、Ｃｒ、Ｍｎ、Ｚｎ、Ｇｅ、Ｈｆの１種または２種以上の元素を１０ｗｔ．％以下の範囲で添加しても良く、本発明の永久磁石は、結晶質の合金粉末を磁場中成形で異方性化した後焼結して得られる焼結異方性永久磁石で、平均結晶粒径が１～５０μｍの範囲にある正方晶系の結晶構造を有する化合物を主相とし、最大エネルギー積が２０ＭＧＯｅ以上に達する。かくして得られた希土類−鉄−ボロン系永久磁石体をリン酸、水酸化ナトリウム等の酸あるいはアルカリ溶液で前処理を行った後、耐食性皮膜を電解めっき、無電解めっき、気相めっき法などの一般的に知られている方法で作製する。その後、不活性雰囲気、非酸化性雰囲気あるいは真空中、４００～６００℃で熱処理をする。耐食性皮膜の形成方法としては、コスト面および皮膜厚さの均一性から電解めっき、無電解めっきが望ましい。また、耐食性皮膜を形成後熱処理し、さらに耐食性皮膜を形成することができる。耐食性皮膜は熱処理により結晶化し脆くなるので、熱処理後さらに耐食性皮膜を形成することにより強度を補うこともできる。熱処理後に耐食性皮膜を形成する場合、リン酸、水酸化ナトリウム等の酸あるいはアルカリ溶液で前処理を行った後、耐食性皮膜を電解めっき、無電解めっき、気相めっき法などの一般的に知られている方法で作製することができる。また、樹脂コート等の皮膜を形成しても良い。

【０００９】

【実施例】以下、本発明を実施例によって具体的に説明するが、本発明はこれらの実施例によって限定されるものではない。

【0010】（実施例1）Nd２３．５wt．％、Pr７．０wt．％、Dy１．５wt．％、Al０．２wt．％、Nb０．６wt．％、B１．０５wt．％、Co２．３wt．％、Ga０．１wt．％、Cu０．０８wt．％、残部Feよりなる磁石合金を不活性雰囲気中で高周波溶解し鋳造インゴットを得た。このインゴットを５０mm角以下に破断した後、破断塊を密閉容器内に挿入しArガスを２０分間流入させて空気と置換し、１kgf／cm2の水素ガスで２時間処理後機械的に粉砕し平均粒子径が５００μmの粉末にした。この粗粉をジェットミルを用いて平均粒子径が５．０μmの粉末に微粉砕した。この微粉をダイス、下パンチで形成される成形空間に充填し、約１０kOeの磁場中で配向させながら、２ton／cm2にて加圧成形し成形体を得た。この成形体を１０８０℃、２時間の条件で焼結し、９００℃、１時間の熱処理を施し永久磁石を作製した。この磁石体から１０×１１×８mm（磁化方向：８mm）の試料を切り出し表面研磨後、リン酸により前処理を行いワット浴を用いて、平均厚み２０μmの電解Niめっきを行った。このNiめっき膜を形成した試料をArガス雰囲気中で、４６０～５２０℃、１時間の熱処理を行った後、磁気特性および加熱温度に対する不可逆減磁率の変化を測定した。図１に熱処理温度に対する保磁力の変化、図２に加熱温度に対する不可逆減磁率の変化を示す。表１に４８０℃で熱処理した試料の QUAD SEVASTIANV によるNiめっき膜の密着強度を示す。図１より、本発明例である実施例１は、熱処理温度が４６０～５００℃の範囲で高い保磁力が安定して得られることがわかる。また、図２より、実施例１は、比較例２、３に比し、高温での不可逆減磁率の低下が少ないことがわかる。

【0011】（比較例1）Nd２３．５wt．％、Pr７．０wt．％、Dy１．５wt．％、Al０．２wt．％、Nb０．６wt．％、B１．０５wt．％、Co２．３wt．％、Ga０．１wt．％、残部Feよりなる磁石合金を不活性雰囲気中で高周波溶解し鋳造インゴットを得た。このインゴットを５０mm角以下に破断した後、破断塊を密閉容器内に挿入しArガスを２０分間流入させて空気と置換し、１kgf／cm2の水素ガスで２時間処理後機械的に粉砕し平均粒子径が５００μmの粉末にした。この粗粉をジェットミルを用いて平均粒子径が５．０μmの粉末に微粉砕した。この微粉をダイス、下パンチで形成される成形空間に充填し、約１０kOeの磁場中で配向させながら、２ton／cm2にて加圧成形し成形体を得た。この成形体を１０８０℃、２時間の条件で焼結し、９００℃、１時間の熱処理を施し永久磁石を作製した。この磁石体から１０×１１×８mm（磁化方向：８mm）の試料を切り出し表面研磨後、リン酸により前処理を行いワット浴を用いて、平均厚み２０μmの電解Niめっきを行った。このNiめっき膜を形成した試料をArガス雰囲気中で、５００～５５０℃、１時間の熱処理を行った後、磁気特性および加熱温度に対する不可逆減磁率の変化を測定した。図１に熱処理温度に対する保磁力の変化を示す。表１に５２０℃で熱処理した試料の QUAD SEVASTIAN V によるNiめっき膜の密着強度を示す。図１より、比較例１は、熱処理温度に対する保磁力の変化が大きいことがわかる。

【0012】（比較例2）Nd２３．５wt．％、Pr７．０wt．％、Dy１．５wt．％、Al０．２wt．％、Nb０．６wt．％、B１．０５wt．％、Co２．３wt．％、Ga０．１wt．％、Cu０．０８wt．％、残部Feよりなる磁石合金を不活性雰囲気中で高周波溶解し鋳造インゴットを得た。このインゴットを５０mm角以下に破断した後、破断塊を密閉容器内に挿入しArガスを２０分間流入させて空気と置換し、１kgf／cm2の水素ガスで２時間処理後機械的に粉砕し平均粒子径が５００μmの粉末にした。この粗粉をジェットミルを用いて平均粒子径が５．０μmの粉末に微粉砕した。この微粉をダイス、下パンチで形成される成形空間に充填し、約１０kOeの磁場中で配向させながら、２ton／cm2にて加圧成形し成形体を得た。この成形体を１０８０℃、２時間の条件で焼結し、９００℃と４８０℃、１時間の熱処理を施し永久磁石を作製した。この磁石体から１０×１１×８mm（磁化方向：８mm）の試料を切り出し表面研磨後、リン酸により前処理を行いワット浴を用いて、平均厚み２０μmの電解Niめっきを行った。図２に加熱温度に対する不可逆減磁率の変化を示す。表１に QUAD SEVASTIAN V によるNiめっき膜の密着強度を示す。図２より、本発明例である実施例１は、比較例２に比し、高温での不可逆減磁率が良好であることがわかる。

【0013】

【表１】

| | |
|---|---|
| 実施例１ | ５３０ kgf／cm2 |
| 比較例１ | ５２５ kgf／cm2 |
| 比較例２ | ３０ kgf／cm2 |

【0014】（比較例3）Nd２３．５wt．％、Pr７．０wt．％、Dy１．５wt．％、Al０．２wt．％、Nb０．６wt．％、B１．０５wt．％、Co２．３wt．％、Ga０．１wt．％、Cu０．０８wt．％、残部Feよりなる磁石合金を不活性雰囲気中で高周波溶解し鋳造インゴットを得た。このインゴットを５０mm角以下に破断した後、破断塊を密閉容器内に

挿入しＡｒガスを２０分間流入させて空気と置換し、１ｋｇｆ／cm2の水素ガスで２時間処理後機械的に粉砕し平均粒子径が５００μｍの粉末にした。この粗粉をジェットミルを用いて平均粒子径が５．０μｍの粉末に微粉砕した。この微粉をダイス、下パンチで形成される成形空間に充填し、約１０ｋＯｅの磁場中で配向させながら、２ｔｏｎ／ｃm2にて加圧成形し成形体を得た。この成形体を１０８０℃、２時間の条件で焼結し、９００℃と４８０℃、１時間の熱処理を施し永久磁石を作製した。この磁石体から１０ｘ１１ｘ８mm（磁化方向：８mm）の試料を切り出し表面研磨後、リン酸により前処理を行いワット浴を用いて、平均厚み２０μｍの電解Ｎｉめっきを行った。このＮｉめっき膜を形成した試料をＡｒガス雰囲気中で、２００℃、１時間の熱処理を行った後、加熱温度に対する不可逆減磁率の変化を測定した。図２に加熱温度に対する不可逆減磁率の変化を示す。図２より、めっき膜形成後に２００℃で熱処理を行った比較例３は、めっき膜形成後に熱処理を行わない比較例２と不可逆減磁率が同等であり、２００℃程度の熱処理では不可逆減磁率向上の効果が得られないことがわかる。

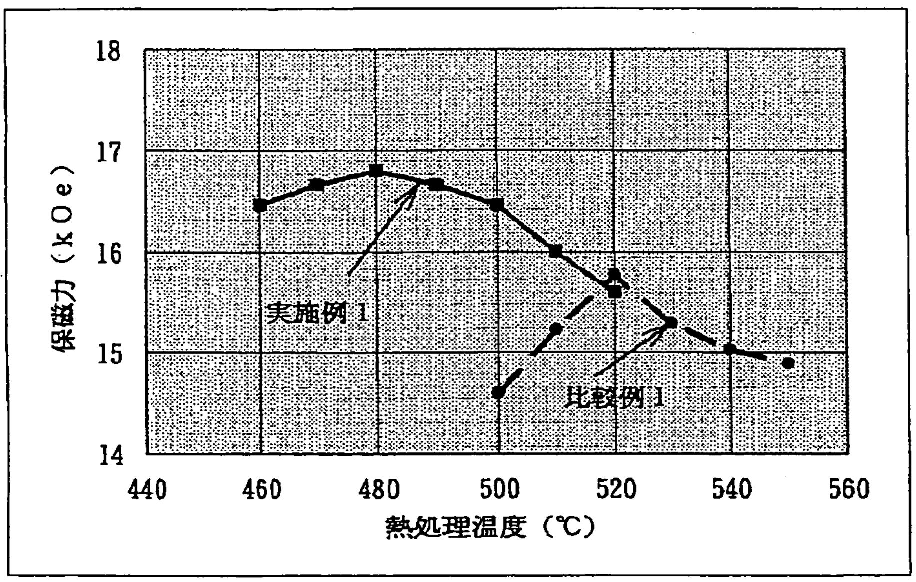
【発明の効果】本発明によれば、温度特性および耐食性を向上させたＲ－Ｆｅ－Ｂ系永久磁石に耐食性皮膜を形成し、不活性雰囲気、非酸化性雰囲気あるいは真空中、４００～６００℃で熱処理することにより、切削加工あるいは電解めっき等で劣化した結晶組織部を修復させ、磁気特性の劣化および磁気特性の経年変化を改善すると共に、コーティング膜と磁石体との密着性をも向上させることができ、工業上その利用価値は極めて高いものである。

【図面の簡単な説明】

【図１】めっき膜形成後の熱処理温度に対する保磁力の変化を示す図である。

【図２】加熱温度に対する不可逆減磁率の変化を示す図である。

【図１】



【図２】